

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

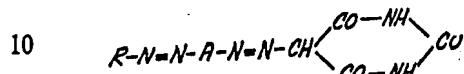
Polyazo-Dyestuffs derived from Barbituric Acid and process for their manufacture

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

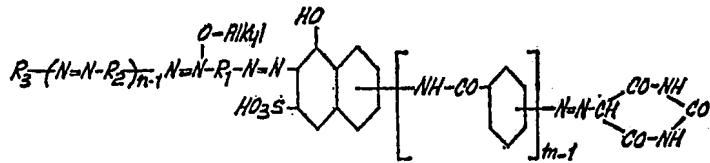
This invention provides valuable new poly-azo-dyestuffs of the general formula

in which R represents the residue of a diazo-component containing at least one azo linkage, and which residue contains in a position vicinal to the —N=N—A— grouping a group capable of taking part in the formation of heavy metal complexes, and A represents the residue of an oxynaphthalene sulphonic acid bound to the R—N=N— group in a position vicinal to the hydroxyl group, and also provides complex heavy metal compounds, especially complex copper compounds, of the polyazo-dyestuff of the above formula.

More especially the invention provides polyazo-dyestuffs of the general formula



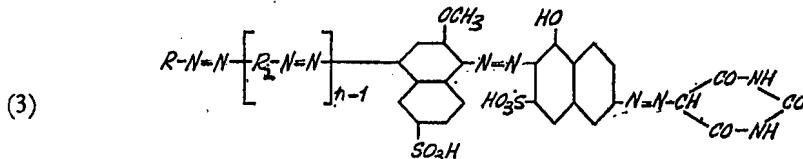
(1)



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(2)

in which n and m each represent the positive whole number 1 or 2, and R_1 and R_3 each represent a benzene or naphthalene nucleus and R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue; of special value are polyazo-dyestuffs of the formula 2,

in which $n=2$, $m=1$ and R_2 represents a 5-pyrazolone residue which is bound in the 4-position to the $R_3-N=N-$ group and in the 1-position through an arylene group to the $-N=N-R_1-$ group and preferably polyazodyestuffs of the formula



40 in which n is the whole number 1 or 2, R represents a benzene or naphthalene nucleus, and R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue.

The invention also provides a process for the manufacture of the dyestuffs of the above

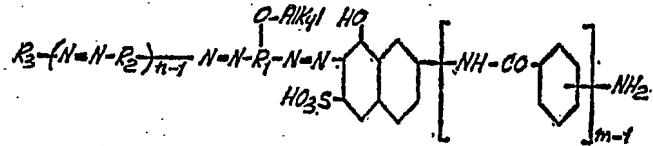
[Price 4s. 6d.]

general formula (1), wherein barbituric acid is coupled with a diazo compound of an amino-polyazo-dyestuff of the general formula

$$(4) \quad \text{R}-\text{N}=\text{N}-\text{A}-\text{NH}_2,$$

or of a complex heavy metal compound of such dyestuff, in which formula R represents the residue of a diazo-component containing at least one azo linkage, and which residue 10
 5 contains in a position vicinal to the $-N=N-A-$ grouping a group capable of taking part in the formation of heavy metal complexes, and A represents the residue of an oxynaphthalene sulphonic acid bound

In particular the invention also provides a process wherein barbituric acid is coupled with a diazo-compound of an amino-azo-dyestuff of the general formula 15

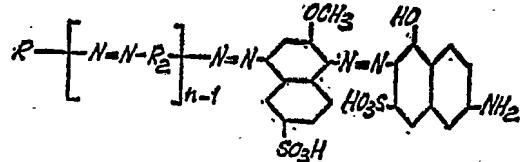


(5)

20 in which n and m each represent the positive whole number 1 or 2, R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue, and R_1 and R_2 each represent benzene or naphthalene nuclei and which advantageously contains copper bound in complex union. The invention furthermore provides such a process, 30
 25 wherein there is used a dyestuff of the formula

5, in which $n=2$, $m=1$ and R_2 represents a 5-pyrazolone residue which is bound in the 4-position to the $R_3-N=N-$ group and in the 1-position through an arylene group to the $-N=N-R_1$ grouping and particularly a process, wherein there is used as diazo-component a diazo-compound of a dyestuff of the general formula

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(6)

in which R represents a benzene or naphthalene residue, R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue, and n is the whole number 1 or 2.
 40 The metal-free dyestuffs of the formula (2) used as starting materials can be obtained by coupling an aminonaphthol sulphonic acid (for example, 2 - amino - 5 - oxynaphthalene - 7 - sulphonic acid, 2 - amino - 6 - oxynaphthalene - 8 - sulphonic acid, 2 - amino - 8 - oxynaphthalene - 6 - sulphonic acid or 1 - amino - 8 - oxynaphthalene - 3:6 or -4:6 - disulphonic acid) in a position vicinal to the hydroxyl group with a diazo-compound of an amino-azo-dyestuff of the formula $R-NH_2$, which contains in a position vicinal to the diazo-group a grouping capable of taking part in the formation of metal complexes, for example, a carboxyl group or a hydroxyl group that may be etherified.

45 Instead of the aforesaid aminonaphthol sulphonic acids, which contain the amino group bound directly to the naphthalene nucleus, there may be used aminonaphthol sulphonic acids which contain this diazotisable amino group in an external nucleus, for example, in a benzoyl residue. As examples of such aminonaphthol sulphonic acids there may be mentioned 2 - (4¹ - aminophenyl-amino) - 5 - oxynaphthalene - 7 - sulphonic acid and more especially 2 - (4¹ - amino-

benzoylamo) - 5 - oxynaphthalene - 1 - sulphonic acid.

50 As diazotised amino-azo-dyestuffs there may be mentioned diazo-compounds of amino-monoazo as well as amino-disazo-dyestuffs, which can be made by the usual methods, for example, by coupling any desired diazo-compound with a coupling component containing a free amino group and containing in a position vicinal to the free amino group a grouping capable of taking part in the formation of metal complexes, for example, with a 2-alkoxy - 1 - aminobenzene unsubstituted in the 4-position, such as 2 - methoxy - 1 - aminobenzene, 2 - methoxy - 5 - methyl - 1 - aminobenzene, 2:5 - dimethoxy- or 2:5 - diethoxy- 1 - aminobenzene or the like, or with a 2-alkoxy- or 2-carboxymethoxy-1-aminonaphthalene derivative, such as a 2 - methoxy - 1 - aminonaphthalene monosulphonic acid unsubstituted in the 4-position. As diazo-components to be coupled with such coupling components for making the starting compounds of the formula $R-NH_2$ there may be mentioned:

55 (a) Simple benzene or naphthalene derivatives: aminosalicylic acid, aminobenzoic acids, aminobenzene - ortho-, -meta- or -para-sulphonic acid, 1 - aminobenzene - 2;5 - disulphonic acid, 4 - chloro - 1 - aminobenzene - 2 - sulphonic acid, and also nitro- or chloro-

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5 anilines, 4 - amino - 4¹ - acetylaminodiphenyl-
3 - sulphonic acid, 1 - aminonaphthalene-3:6-
disulphonic acid, 2 - aminonaphthalene - 4:8-
disulphonic acid or dehydrothiotoluidine mono-
or di-sulphonic acids;

10 (b) Amines containing azo linkages, such
as amino-azobenzene mono- or di-sulphonic
acid, and those obtainable by coupling a
(a) with a coupling component containing
a diazotisable amino group, such as 3-methyl-
aniline, 1-aminonaphthalene-6- or -7-sulphonic
acid and also the coupling components men-
tioned above that contain amino groups, and
15 also those obtainable by coupling a diazo-
compound of a monoacylated diamine with
any desired coupling component and subse-
quently hydrolysing the acylamino group to
20 form a free amino group.

25 Useful amino-azo-dyestuffs of the formula
(2) can be obtained by coupling a tetrazo-
tised diamine, which contains in a position
vicinal to the diazo-group a grouping capable
30 of taking part in the formation of metal com-
plexes, for example, by coupling tetrazotised
4:4¹ - diamino - 3:3¹ - dimethoxy - diphenyl,
on the one hand, with an aminonaphthol sul-
phonic acid capable of coupling in a position
35 vicinal to the hydroxyl group and, on the other,
with any desired coupling component, and
advantageously one capable of forming metal
complexes.

40 As diazo-components to be coupled with the
aforesaid coupling components for making the
starting compounds of the formula R—NH₂,
there may also be used the complex metal
compounds thereof which are obtainable by
the metallisation of monoazo-dyestuffs obtain-
able, for example, from 1 - aminophenyl- 3-
methyl - 5 - pyrazolones, 1 - aminophenyl-
3 - carboxy - 5 - pyrazolones, 1 - amino-
stilbenyl - 3 - methyl - 5 - pyrazolone - 2¹:
2¹¹ - disulphonic acid and diazotised ortho-
45 aminophenols and sulphonic acids thereof or
diazotised ortho-aminobenzoic acids and sul-
phonic acids thereof.

50 The dyestuffs of the formula (2) can be
made by the usual known methods. The initial
components are advantageously coupled with
the aminonaphthol sulphonic acids in an alka-
line medium. Before or preferably after the
diazotisation and coupling of the amino-azo-
dyestuffs so obtained, of which a large number
55 is known (see for example, those described
and claimed in Specification No. 744,666),
with barbituric acid, they may be converted
into complex metal compounds thereof. As
agents yielding metal there may be used, for
example, agents yielding nickel but preferably
60 agents yielding copper. The treatment with
the agent yielding metal is advantageously
carried out in such manner that a complex
metal compound of an ortho-carboxy - ortho¹-
oxy or ortho: ortho¹ - dioxy - azo - dyestuff is
65 formed, that is to say, in such manner that

any alkoxy group present in ortho-position
to the azo linkage is split up and one atom
of metal is bound in complex union, for
example, with one ortho: ortho¹ - dioxy - azo-
grouping or one ortho - oxy - ortho¹ - carb-
oxy - azo - grouping.

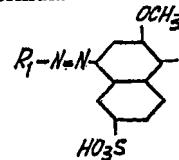
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The treatment with the agent yielding metal
is therefore carried out in such manner that
an ortho: ortho¹ - dioxy - azo - copper com-
plex is formed, when the metallisable group-
ing is an ortho: ortho¹ - dioxy - azo- or ortho-
oxy - ortho¹ - alkoxy - azo - grouping. As
is known this reaction takes place more easily
with an ortho: ortho¹ - dioxy - azo - grouping
than with an ortho - oxy - ortho¹ - alkoxy-
azo - grouping, so that in the latter case a
longer period of reaction and/or a higher
temperature is required. The metallisation is
carried out, for example, with a salt of divalent
copper or nickel in a weakly acid aqueous
medium. The dyestuffs can also be metallised
by the known method in which the metallisa-
tion is carried out in an aqueous medium
advantageously for several hours in the vicinity
of 100° C. with the use of a nickel- or copper-
tetramine complex in the presence or absence
of an excess of amine or ammonia. Of special
advantage in some of these cases is the process
described and claimed in Specification No.
644,883, which is carried out in the presence
of an oxyalkylamine, especially ethanolamine,
or a copper complex derived therefrom.

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80 Useful amino-azo-dyestuffs of the general formula (2)
which contain in a position vicinal to the azo
linkage connecting R with A an alkoxy group
bound to a naphthalene residue, for example,
dyestuffs of which the residue R in the formula
(2) has the formula

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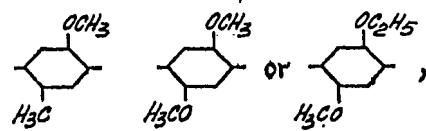
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95 in which R₁ represents the residue of any de-
sired diazo-component, are in general advan-
tageously coppered with copper sulphate in
the presence of an alkali metal acetate.

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105 On the other hand, those dyestuffs which
contain at the aforesaid position in the mole-
cule an alkoxybenzene residue, for example,
a residue of the formula

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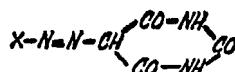
115 are advantageously converted into the ortho: ortho¹-dioxy-copper complex by means of a copper-tetramine sulphate.

The metalliferous dyestuffs so obtained are
also largely known and correspond to the

formula (2).

The diazo-compounds obtained from the amino-azo-dyestuffs of the formula (2) or their complex metal compounds are coupled with barbituric acid to form the dyestuffs of the formula (1), advantageously in a weakly alkaline medium. The dyestuffs so obtained, which contain no heavy metal in complex union, can be metallised, for example, by the methods described above for metallising the starting dyestuffs of the formula (2).

The dyestuffs of this invention, that have the formula (1), can also be made by a modification of the process described above, wherein a diazotised amino-azo-dyestuff, which contains in a position vicinal to the diazo group a grouping capable of taking part in the formation of metal complexes, for example, a hydroxyl, alkoxy or carboxyl group, is coupled with a monoazo-dyestuff of the formula



(4)

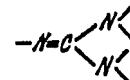
in which X represents the residue of an oxy-naphthalene sulphonic acid capable of coupling in a position vicinal to the hydroxyl group and bound directly to the azo linkage, and, if desired, the polyazo-dyestuff so obtained is converted into a complex heavy metal compound thereof.

For making the dyestuffs of the formula (4) there may be used as diazo-components the amino-naphthol sulphonic acids mentioned above for use as coupling compounds in making the dyestuffs of the formula (2) and as coupling components amino-naphthol sulphonic acids. As amino-azo-dyestuffs to be coupled with the dyestuffs of the formula (4) there are used in this modification of the process the products obtainable by the methods described above for making the compounds of the formula R—NH₂.

The polyazo-dyestuffs of this invention are suitable for dyeing or printing a very wide variety of materials, for example, those of animal origin, such as wool, silk or leather, and especially for dyeing or printing cellulosic materials, such as cotton, linen, artificial silk or staple fibres of regenerated cellulose. Those dyestuffs that contain no heavy metal or contain a metallisable group may be treated on the fibre or in the dyebath with an agent yielding a heavy metal, advantageously an agent yielding copper.

55 In some cases especially valuable dyeings are obtained by using the process in which a dyeing or print produced with the metal-free dyestuff is after-treated with an aqueous solution which contains a water-soluble, and

especially complex, copper compound and a basic formaldehyde condensation product of a compound containing at least once an atomic grouping of the formula



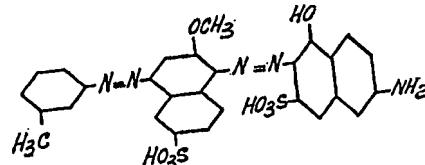
for example, dicyandiamide or dicyandiamidine, or a compound, for example, cyanamide, that is easily convertible into a compound containing such an atomic grouping. Such a process is described and claimed, for example, in Specification No. 619,969.

The dyeings produced with the new dye-stuffs in the manner described above are usually distinguished by their good properties of wet fastness, and especially their very good fastness to light and good capacity for being discharged.

The following Examples illustrate the invention, the parts and percentages being by weight:

EXAMPLE 1.

6. 2 parts of the disazo-dyestuff of the 80 formula



are dissolved in 100 parts of warm water in the form of the sodium salt. The solution is cooled to 5-10° C., 0.7 part of sodium nitrite is added dissolved in water, and then 4 parts of hydrochloric acid of 30% strength are added, diluted with a small amount of water, the whole is stirred for a few hours, while cooling, and then coupling is carried out with a solution of 1.3 parts of barbituric acid rendered alkaline with sodium carbonate. When the coupling is complete 5 parts of sodium chloride are added for every 100 parts by volume of solution, and the precipitated dyestuff is filtered off. By heating the precipitate for several hours in a weak acetic acid solution with copper acetate the complex copper compound is made in known manner. The latter compound is dried, and is a green-black powder which dissolves in water with a green coloration, and yields green dyeings on cotton or viscose.

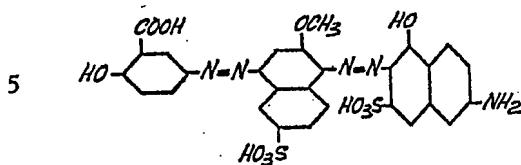
Similar dyestuffs are obtained by using, instead of the dyestuff obtained from 1-amino-3-methylbenzene, one of the dyestuffs of the formulae given in column I of the following Table, in which are given in column II the tints of the dyeings produced on cotton with the finished cupriferous barbituric acid-dyestuff. 110

	I	II
1		bluish green
2		"
3		"
4		"
5		green
6		"
7		bluish green

	I	II.
8		bluish green
9		"
10		"
11		green
12		bluish green
13		"

EXAMPLE 2.

6.7 parts of the disazo-dyestuff of the formula



are dissolved in the form of the sodium salt in 75 parts of warm water. The solution is cooled to 5-10° C., 0.7 part of sodium nitrite, dissolved in water, is added, and then 4 parts

of hydrochloric acid of 30% strength, diluted with a little water, are added, and the whole is stirred in the cold for a few hours. Coupling is then carried out with 1.3 parts of barbituric acid in a solution rendered alkaline with sodium carbonate. When the coupling is finished the precipitated trisazo-dyestuff is filtered off, and converted in acetic acid solution into its complex copper compound by heating it with copper acetate in known manner. When dry, the copper complex compound is a green-black powder which dissolves in water with a green coloration, and yields green dyeings on cotton or viscose, which are fast to washing

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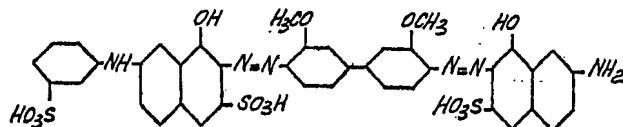
when after-treated with copper salts.

Similar dyestuffs are obtained by using,

instead of the starting dyestuff of the above formula, the following disazo-dyestuffs.

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EXAMPLE 3.
9 Parts of the disazo-dyestuff of the formula

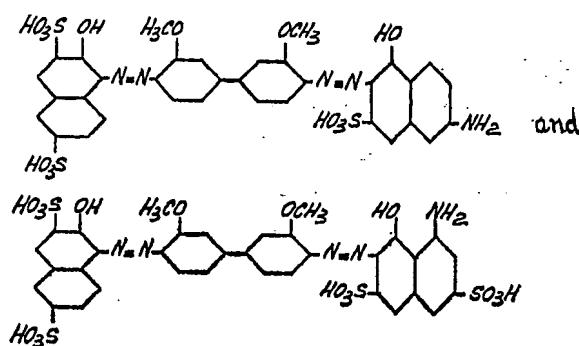


10 are dissolved in the form of the sodium salt in 450 parts of hot water. The solution is then cooled with ice to about 5° C., 0.7 part of sodium nitrite, dissolved in a small amount of water, is added, and diazotisation is brought about by adding 5 parts of hydrochloric acid 15 of 30% strength. The whole is stirred for a few hours, while cooling, and then coupling is carried out with 1.3 parts of barbituric acid in a solution rendered alkaline with sodium carbonate. When the coupling is complete the 20 trisazo-dyestuff formed is precipitated by the addition of sodium chloride, the dyestuff is

filtered off and then converted into its complex copper compound in known manner by heating it with an ammoniacal solution of copper oxide, if desired, in the presence of a small amount of pyridine. The complex copper compound, when dry, is a blackish grey powder which dissolves in water to give a dull blue coloration. It dyes cotton or viscose 25

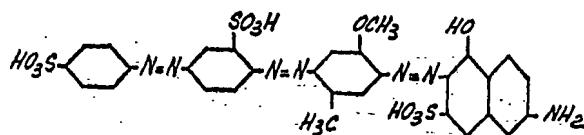
grey tints.

Grey-dyeing complex copper compounds are 30 obtained in a similar manner from the dyestuffs of the formulae



EXAMPLE 4.

7.9 Parts of the trisazo-dyestuff of the formula



5 are dissolved in the form of the sodium salt in 100 parts of hot water and cooled by the addition of ice to 5—10° C. 0.7 Part of sodium nitrite in aqueous solution and 4.5 parts of hydrochloric acid of 30% strength diluted with a little water are added, and 10 the whole is stirred for a few hours in the cold. Coupling with 1.3 parts of barbituric acid is then carried out in a solution rendered alkaline with sodium carbonate. When the coupling is finished the precipitated dyestuff is filtered off, and converted into its complex copper compound in known manner by heating it with an ammoniacal solution of copper oxide. The complex copper compound, when dry, is a blackish powder which dissolves in water with a green coloration, and dyes cotton 15 blackish olive-grey tints.

Similar dyestuffs are obtained by using as starting materials the following dyestuffs: 20

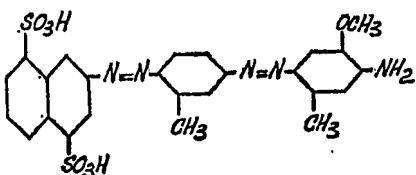
1		Blackish olive-green
2		olive-green
3		olive-green
4		greyish olive
5		green

6		green
7		blackish olive-green
8		olive
9		green
10		green
11		green

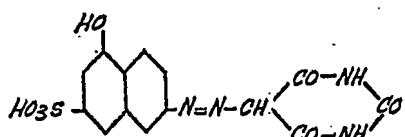
5 In the case of dyestuffs derived from 1-amino-2-methoxynaphthalene sulphonic acids the coppering is advantageously carried out in an acetic acid medium. The sequence of

the operations can generally be varied, for example, dyestuff No. 1 in the Table can equally well be prepared by coupling the disazo-dyestuff of the formula

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with the monoazo-dyestuff of the formula

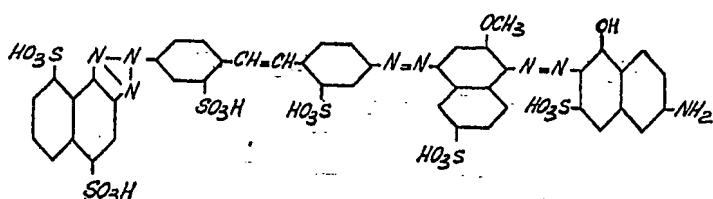


or by carrying out the coppering before the final coupling operation with barbituric acid.

EXAMPLE 5.

12.2 Parts of the disazo-dyestuff of the formula

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10 are dissolved as the sodium salt in 120 parts of water. At 5—10° C. an aqueous solution of 0.7 part of sodium nitrite and 3.5 parts of hydrochloric acid of 30% strength, diluted with a little water, are added. The diazotisation finishes rapidly. Coupling with 1.3 parts of barbituric acid is then carried out in a solution rendered alkaline with sodium carbonate, while cooling. The trisazo-dyestuff precipitates completely. It is filtered off and converted into its complex copper compound in known manner by heating it in a weakly acetic acid solution with copper acetate. The dyestuff dissolves in water with a green colora-

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tion and yields green dyeings on cotton or viscose.

Similar dyestuffs are obtained by using instead of 1 - aminonaphthalene - 4:8 - disulphonic acid to form the triazole, another aminonaphthalene sulphonic acid, such as 1-aminonaphthalene - 3:6 - disulphonic acid, 2 - aminonaphthalene - 5:7 - disulphonic acid, 1 - aminonaphthalene - 4 - sulphonic acid or 2 - aminonaphthalene - 6 - sulphonic acid.

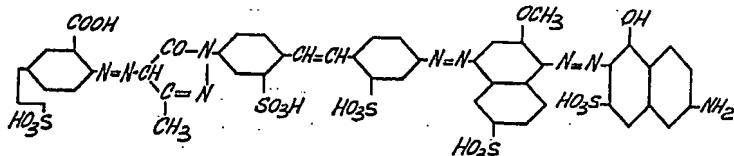
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EXAMPLE 6.

12.3 Parts of the trisazo-dyestuff of the formula

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40 are dissolved as the sodium salt in 180 parts of warm water. The solution is cooled to 5—10° C. and 0.7 part of sodium nitrite is added as an aqueous solution and 4 parts of hydrochloric acid of 30% strength, diluted with a little water, are added. The whole is stirred for a few hours, while cooling, and coupling with 1.3 parts of barbituric acid is then carried out in a solution rendered alkaline with sodium carbonate. The precipitated

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dyestuff is filtered off, and converted into its complex copper compound by heating it in acetic acid solution with copper acetate. The complex copper compound, when dry, is a dark green powder which dissolves in water with a green coloration and yields olive-green dyeings on cotton.

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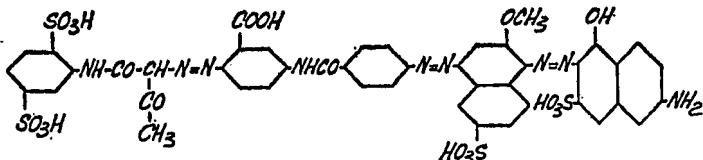
Similar dyestuffs, which dye vegetable fibres green tints, are obtained by using trisazo-dyestuffs of the formulae

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EXAMPLE 7.

11.6 Parts of the trisazo-dyestuff of the formula



5 are dissolved as the sodium salt in 200 parts of water. 0.7 part of sodium nitrite and 4 parts of hydrochloric acid of 30% strength, diluted with a little water, are added, and the whole is stirred in the cold for a few hours. Coupling with 1.3 parts of barbituric acid is then carried out in a solution rendered alkaline with sodium carbonate, and the dyestuff formed is precipitated by adding 10 parts of sodium chloride for every 100 parts by volume of liquor. By heating the precipitate in a weakly acetic acid solution with copper acetate the complex copper compound is prepared in known manner. When dry it is a dark green powder which dissolves in water with a green coloration and yields green dyes on cotton or viscose.

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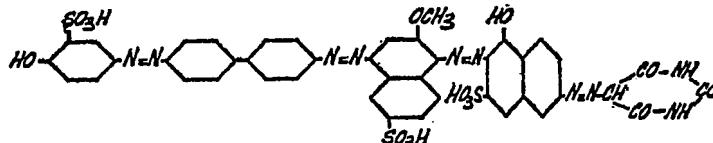
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tetrazotised, then coupled in alkaline solution on one side with 1.8 parts of 1 - oxybenzene-2 - sulphonic acid and then in neutral or weakly acid solution with 2.5 parts of 1-amino - 2 - methoxynaphthalene - 6 - sulphonic acid. When the coupling is finished the disazo-dyestuff obtained is isolated, then diazotised, and coupled in alkaline solution with 2.4 parts of 2 - amino - 5 - oxynaphthalene-7 - sulphonic acid. The trisazo-dyestuff is precipitated by the addition of sodium chloride, then dissolved by the addition of 8 parts by volume of a 2N-solution of sodium hydroxide, and diazotised after the addition of sodium nitrite and hydrochloric acid and a little ice in the usual manner. The product is then coupled with 1.3 parts of barbituric acid in a solution rendered alkaline with sodium carbonate. The complex copper compound of the resulting dyestuff of the formula

1.84 Parts of 4:4¹ - diaminodiphenyl are



45 is obtained by heating the dyestuff for several hours with copper acetate in a weakly acetic acid solution. The copper compound is filtered off and dried, and is then a black powder

which dissolves in concentrated sulphuric acid with a blackish brown coloration and in water with a green coloration. It dyes vegetable fibres olive-green tints that are fast to light.

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EXAMPLE 9.

100 Parts of cotton are entered at 40° C. into a dyebath which contains in 3000 parts of water 1 part of the dyestuff obtainable as 5 described in the first paragraph of Example 1. Dyeing is carried on for half an hour while raising the temperature to 90° C., then 30

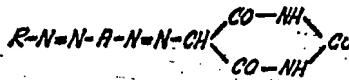
parts of crystalline sodium sulphate are added, and dyeing is continued for a further $\frac{1}{2}$ hour at 90—95° C. The cotton is then rinsed and dried. There is obtained a green dyeing of very good fastness to light.

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WHAT WE CLAIM IS:—

1. Polyazo-dyestuffs of the general formula

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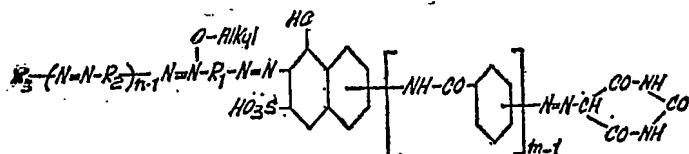
in which R represents the residue of a diazo-component containing at least one azo linkage, and which residue contains in a position vicinal to the $-N=N-A-$ grouping a group capable of taking part in the formation of heavy metal complexes, and A represents the residue of an oxynaphthalene sulphonic acid bound to the $R-N=N-$ group in a position vicinal 20

to the hydroxyl group the naphthalene nucleus of the residue A being advantageously bound directly to the two azo linkages, and complex heavy metal compounds, especially complex copper compounds, of the aforesaid polyazo-dyestuffs.

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2. Polyazo-dyestuffs of the general formula

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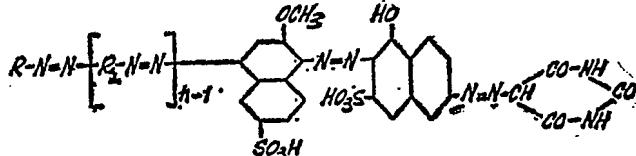
in which n and m each represent the positive 35 whole number 1 or 2, R₁ and R₃ each represent a benzene or naphthalene nucleus and R₂ represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue.

3. Polyazo-dyestuffs as claimed in claim 2,

in which n = 2, m = 1 and R₂ represents a 5-pyrazolone residue which is bound in the 4-position to the R₃—N=N— group and in the 1-position through an arylene group to the $-N=N-R_1-$ group.

40

4. Polyazo-dyestuffs of the formula



45 in which n is the whole number 1 or 2, R represents a benzene or naphthalene nucleus, and R₂ represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue.

50 5. Complex copper compounds of the dyestuffs claimed in claim 2, 3 or 4.

55 6. Any one of the polyazo-dyestuffs of the formula shown in Claim 1 or complex metal compounds thereof obtainable as described in Examples 1—8 and the Tables herein.

70 7. A process for the manufacture of polyazo-dyestuffs, wherein barbituric acid is coupled with a diazo-compound of an amino-polyazo-dyestuff of the general formula



75 60 or of a complex heavy metal compound of

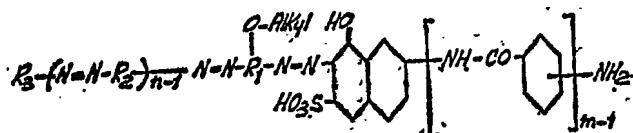
such dyestuff, in which formula R represents the residue of a diazo-component containing at least one azo linkage, and which residue contains in a position vicinal to the $-N=N-A-$ grouping a group capable of taking part in the formation of heavy metal complexes, and A represents the residue of an oxynaphthalene sulphonic acid bound to the azo linkage in a position vicinal to the hydroxyl group, and which residue advantageously contains the $-NH_2$ group bound directly to the naphthalene nucleus.

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8. A process as claimed in claim 7, wherein barbituric acid is coupled with a diazo-compound of an amino-azo-dyestuff of the general formula

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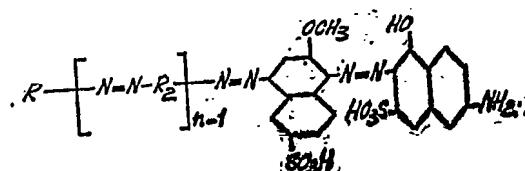
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in which n and m each represent the positive whole number 1 or 2, R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue, and R_1 and R_3 each represent benzene or naphthalene nuclei.

5 9. A process as claimed in claim 7, wherein the barbituric acid is coupled with a diazo-compound of a complex copper compound 10 of a polyazo-dyestuff of the formula given in claim 8.

10 10. A process as claimed in claim 7, 8 or 9, wherein there is used as diazo-component a diazo-compound of a dyestuff of the general 15 formula



in which R represents a benzene or naphthalene residue, R_2 represents a benzene, diphenyl, naphthalene or 5-pyrazolone residue, 20 and n is the whole number 1 or 2.

11. A process as claimed in claim 7, 8 or 9, wherein there is used a dyestuff of the formula given in claim 8, in which $n=2$, $m=1$ and R_2 represents a 5-pyrazolone residue 25 which is bound in the 4-position to the $R_3-N=N-$ group and in the 1-position through

an arylene group to the $-N=N-R_1$ grouping.

12. A modification of the process claimed in any one of claims 7—11, wherein a polyazo-dyestuff of the general formula



in which R represents the residue of a diazo component containing at least one azo linkage, and which residue contains in a position vicinal to the $-N=N-A-$ grouping a group capable of taking part in the formation of heavy metal complexes, and A represents the residue of an oxynaphthalene sulphonic acid bound to the $R-N=N-$ group in a position vicinal to the hydroxyl group, is treated with an agent yielding heavy metal, and especially an agent yielding copper.

13. A dyeing or printing process in which polyazo-dyestuffs of the formula shown in claim 1 or complex metal compounds thereof are used.

10. A dyeing process conducted substantially as described in Example 9 herein.

15. Material which has been dyed or 50 printed by the process claimed in claim 13 or 14.

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